N92-14526

A. Title: Inelastic Collision Processes in Ozone and their Relation to Atmospheric Pressure Broadening

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C Abstract of Research Objectives

This research task employs infrared double-resonance to determine rotational energy transfer rates and pathways, in both the ground and vibrationally excited states of ozone. The resulting data base will then be employed to test inelastic scattering theories and to assess intermolecular potential models, both of which are necessary for the systematization and prediction of infrared pressure-broadening coefficients, which are in turn required by atmospheric ozone monitoring techniques based on infrared remote sensing. In addition, observation of excited-state absorption transitions will permit us to improve the determination of the $2\nu_3$, $\nu_1+\nu_3$, and $2\nu_1$ rotational constants and to derive band strengths for hot-band transitions involving these levels.

D. Summary of Progress and Results

Work on this program, with NASA support, began in March of 1989. Our initial efforts have been directed toward setting up the experimental apparatus necessary for carrying out the double-resonance measurements, acquiring a spectroscopic data base for ozone, and devising a stragegy for theoretical interpretation of the anticipated results. To date, the following tasks have been accomplished:

1) An ozone-compatible vacuum system and double-resonance cell have been assembled, capable of preparing ozone samples of up to 90% purity or in mixtures with buffer gases, and holding these samples at a controlled temperature for a period of time sufficient to carry out experiments.

2) A set of lead-salt diode lasers has been ordered and tested for operation in the 1000 - 1050 cm^{-1} region, corresponding to the $\nu_3 \leftarrow 0$, $2\nu_3 \leftarrow \nu_3$, and $\nu_1+\nu_3 \leftarrow \nu_1$ absorption regions of ozone.

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3) We have received the ozone line listing from NASA Ames Research Center via Bitnet, along with selected portions of the FT-IR absorption spectrum. Since some of the hot-band line-center positions have been revised in the most recent (1989) update, we will need to incorporate these revisions in our database.

4) Transient three-level double resonance signals have been obtained for the $(2\nu_3-\nu_3,\ 18_{4,14} - 17_{4,13})$ transition in ozone when the $(\nu_3-0,\ 17_{4,13} - 16_{4,12})$ transition is pumped with the CO_2 laser at 1053.92 cm^{-1}. Both rotational and vibrational relaxation decays may be observed at different time scales, as shown in Fig. 1. A search is now in progress for additional signals in the ν_3-0, $2\nu_3-\nu_3$, and $\nu_1+\nu_3-\nu_1$, bands, following which the relaxation rates will be measured as a function of ozone and buffer-gas pressures and temperature.

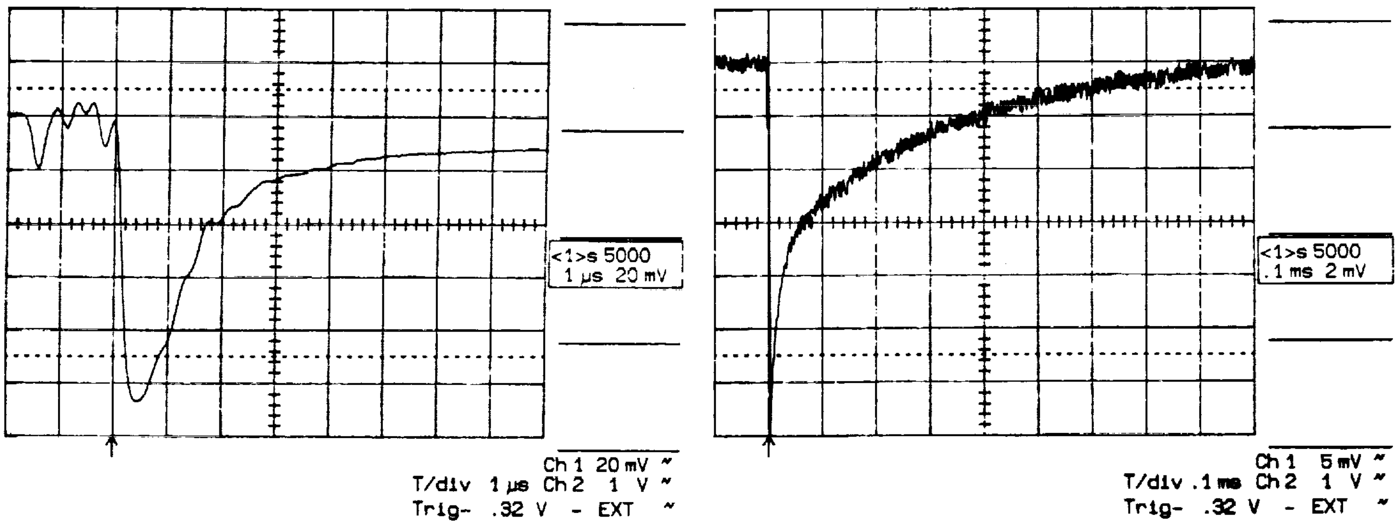

Figure 1. 3-level double-resonance (excited-state absorption) on the $(2\nu_3-\nu_3, 18_{4,14}-17_{4,13})$ transition in ozone (0.25 Torr). The fast decay in the left trace is due to rotational relaxation, while the slower decay, with smaller amplitude, shown in the right-hand trace is due to vibrational relaxation of the rotationally equilibrated $\nu_3=1$ level.

5) Theoretical analysis will focus on validation of the Quantum Fourier Transform (QFT-ID) theory developed by Dr. R. Gamache of the University of Lowell. In initial discussions with Dr. Gamache, we have developed a strategy for extracting final-state-specific transition probabilities from his calculations, which will then be compared with the state-to-state measurements resulting from our experiments.

E. PUBLICATIONS

J. Steinfeld, B. Foy, J. Hetzler, C. Flannery, J. Klaassen, Y. Mizugai, and S. Coy, "Determination of Molecular Spectroscopic Parameters and Energy Transfer Rates by Double Resonance Spectroscopy", Proceedings, Workshop/Conference on Laboratory Research for Planetary Atmospheres (Bowie, Md, Oct. 1989)